Achieving Small Dimensions with an Environmentally Friendly Solvent: Photoresist Development Using Supercritical CO_2

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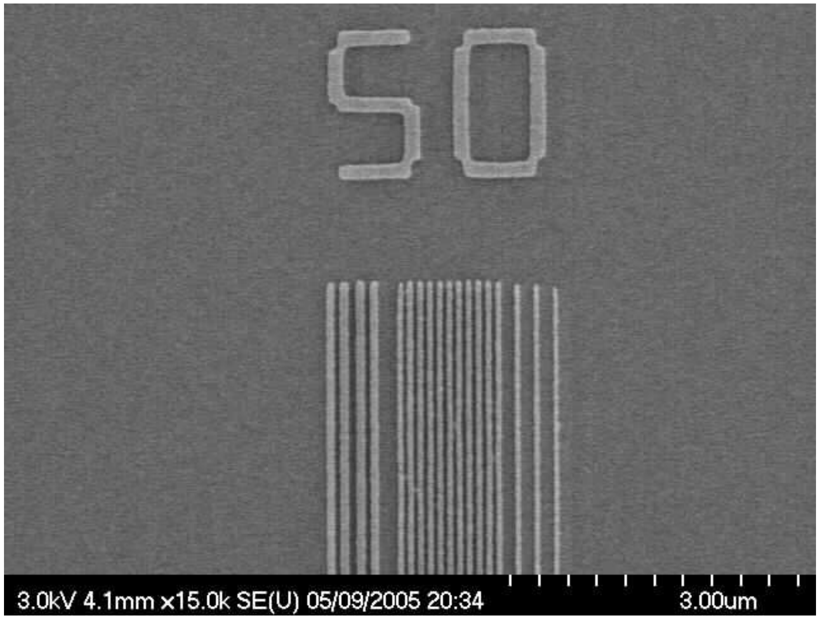
ERC Teleseminar, Nov. 1, 2007

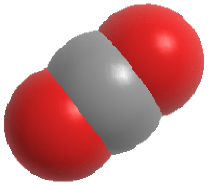
Outline

- Supercritical CO_2 as a development solvent
  - Advantages
  - Use with polymeric photoresist systems
- Small molecule photoresists
  - Potential advantages
  - Solubility in $scCO_2$
  - Patterning performance

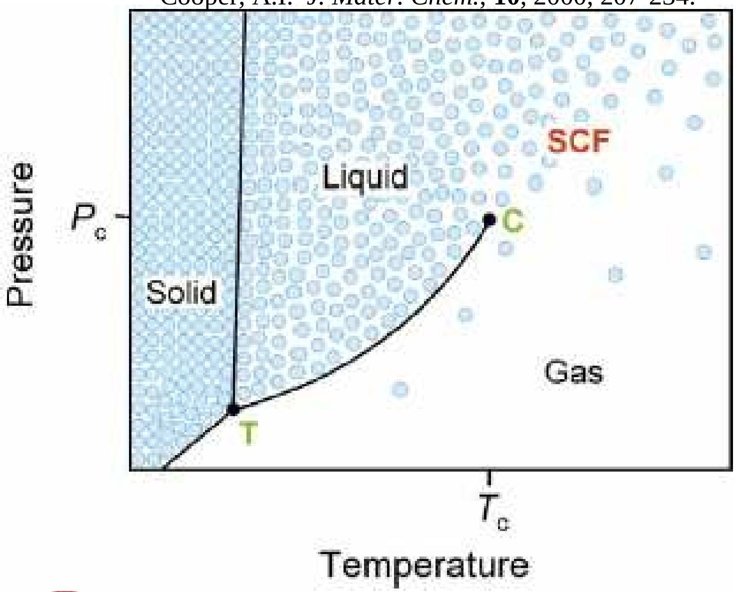


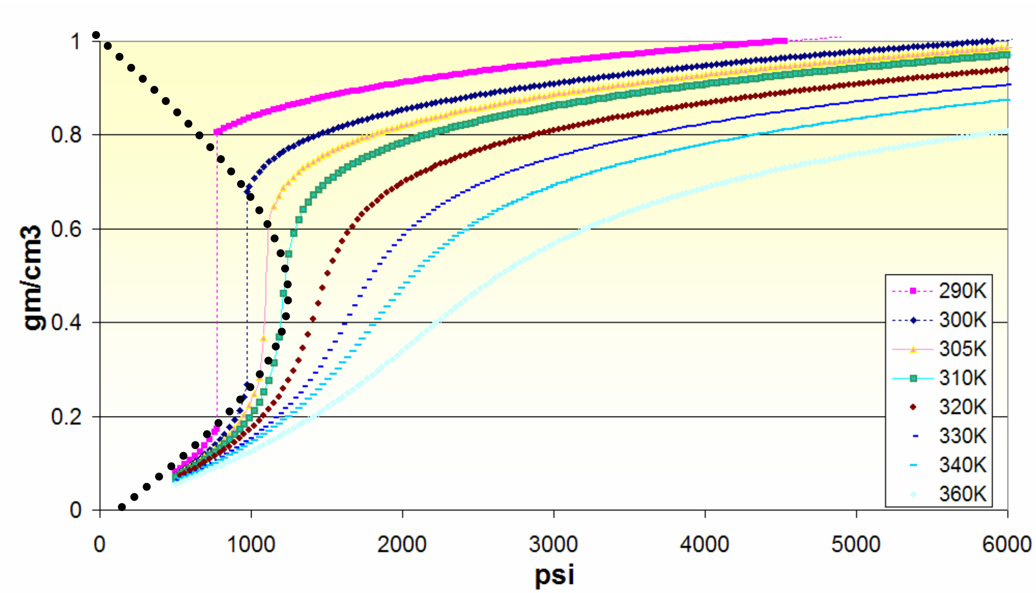
Supercritical CO_2 Basics

- Supercritical CO_2
  - Tunable, non-polar solvent with the ability to dissolve select non-polar materials
  - T_c = 31C, P_c = 1070psi (77 bar)



Cooper, A.I. *J. Mater. Chem.*, **10**, 2000, 207-234.

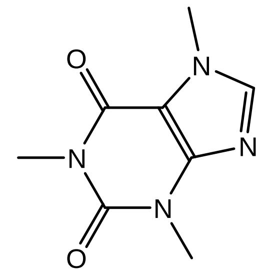




Supercritical CO_2 in Industry

Flavex®

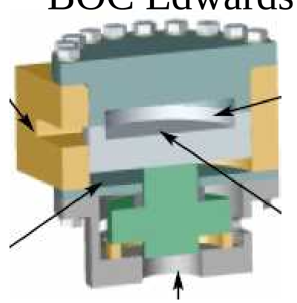
- Extraction of essential oils from organic matter
  - Cinnamon, ginger, sandalwood, etc
  - Pharmaceutical applications



- Decaffeination of coffee
  - CO_2 replaced CH_2Cl_2 as solvent, removed only caffeine
- Dry Cleaning
  - Addition of surfactants

Hangers CLEANERS

BOC Edwards

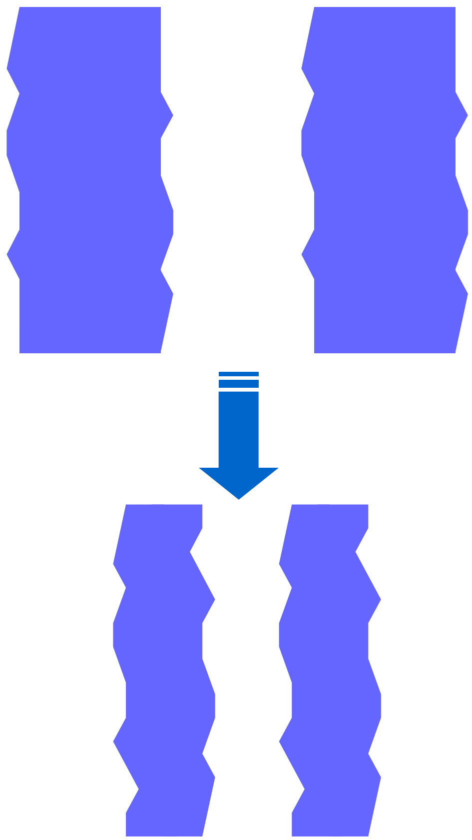


- **Wafer cleaning**
  - BOC Edwards DFP-200
  - Critical Point Dryer

Next Generation Lithography: Key Problems

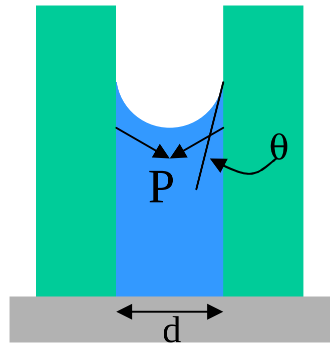
Pattern Variations

< 3nm for 32nm node



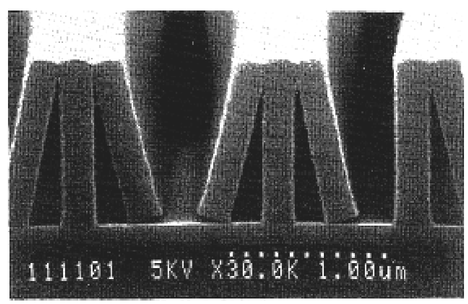
Pattern Collapse

Reduce surface tension



$$P = \frac{\sigma}{R} = \frac{2\sigma\cos\theta}{d}$$

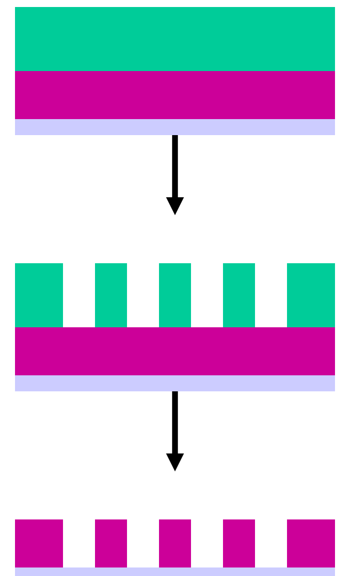
@ 50nm L/S, aspect ratios >2:1 collapse w/water



T. Tanaka, M. Morigami, N. Atoda, *JJAP*, **32**(pt1, 12B) 6059 (1993).

Non-polar Materials

Low-κ applications



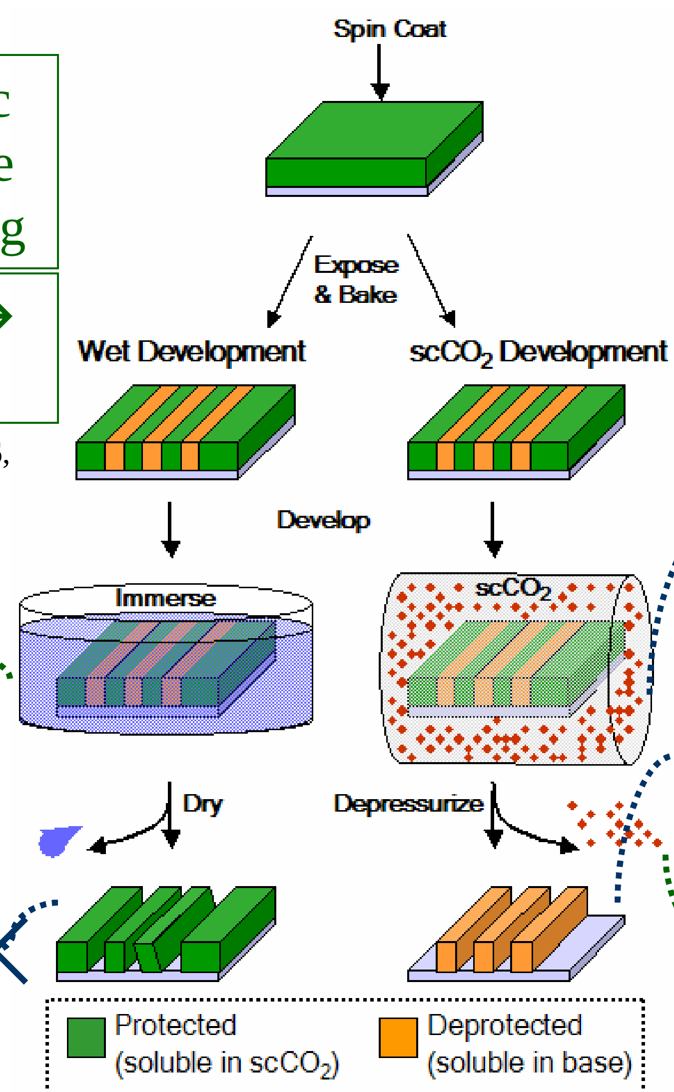
Lack of appropriate non-polar developers → Must use mulitple subtractive steps

Advantages of Supercritical CO_2 Development

Elimination of organic solvents and ultra-pure water during processing

2 gram DRAM chip → 32 kg of water

Williams, et al., *Environ. Sci. Tech.*, **36**, 5504, (2002).



Liquid-like density, Tunable Solvating Power

Gas-like transport

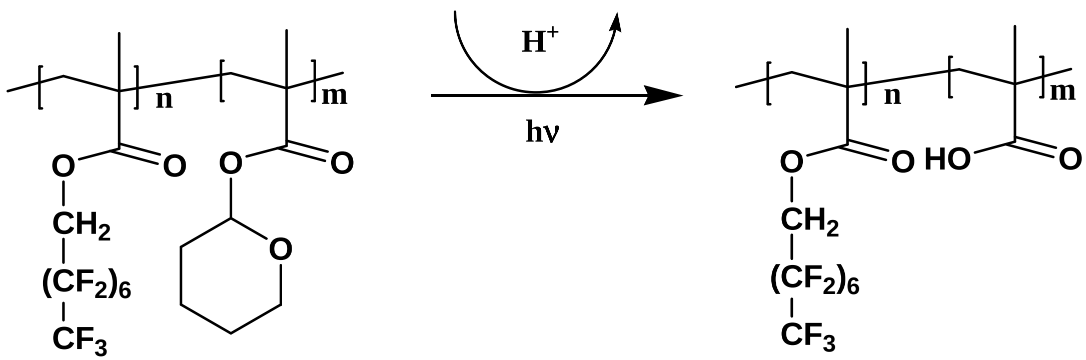
Penetrates crevices, no residue

No surface tension, eliminates pattern collapse

Harmful solvents are cleanly separated via depressurization

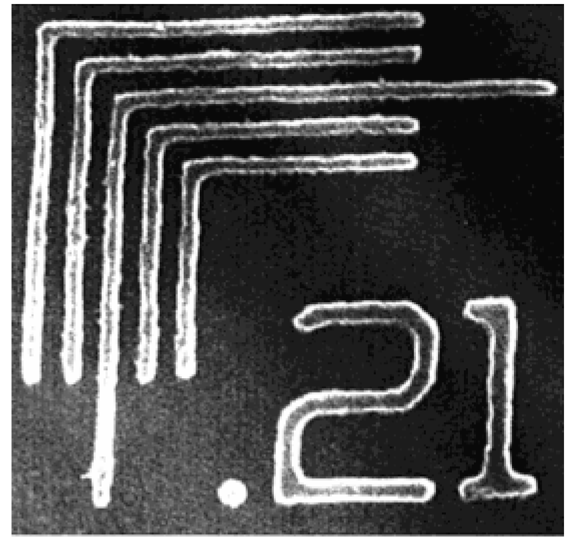
Fluorinated scCO2 Soluble Photoresists

- First platform for soluble polymeric photoresists
  - Copolymerize traditional photoresist monomers with fluorinated monomers
- Negative tone



Soluble

Insoluble



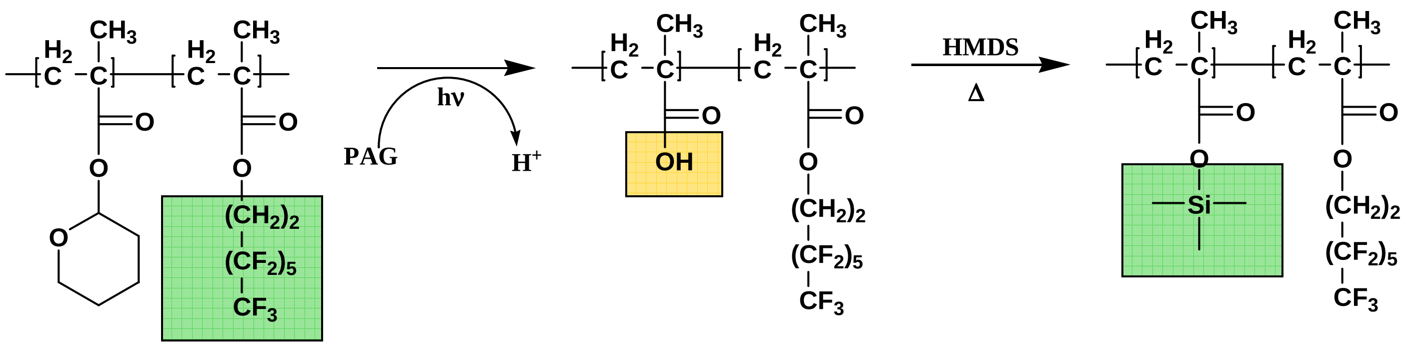
Sundararajan, et al. 193 nm exposure.

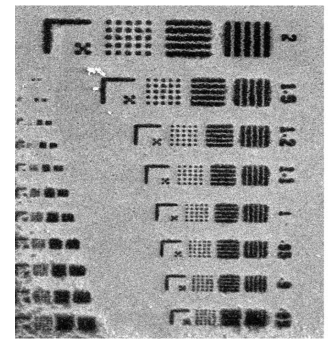
- Block copolymer (Cornell) and random copolymer (UNC) versions demonstrated.

N. Sundararajan, S Yang, K Oglno, S Vallyaveettfl, J Wang, X Zhou, C. K. Ober, S. K. Obendorf, and R. D. Allen, *Chem. Mater.* 12, 41 (2000).
D. Flowers, E N Hogan, R Carbonell, mad J. M. DeSlmone, in Proceedings of SPIE, 4690, 419 (2002).

Positive Tone Resists for $scCO_2$ Development

Two-step positive-tone





Pham, V Q.. et al., *Chem. Mater.* 15(26), 2003, 4893-5.

- Balance must be struck between resist solubility (increase F) and contrast (increase functionality)

Resist Fluorination

- Advantages
  - High transparency at 193 nm, 157 nm exposure wavelengths
    - Library of fluorinated monomers
  - Simple to increase scCO2 solubility with monomer inclusion

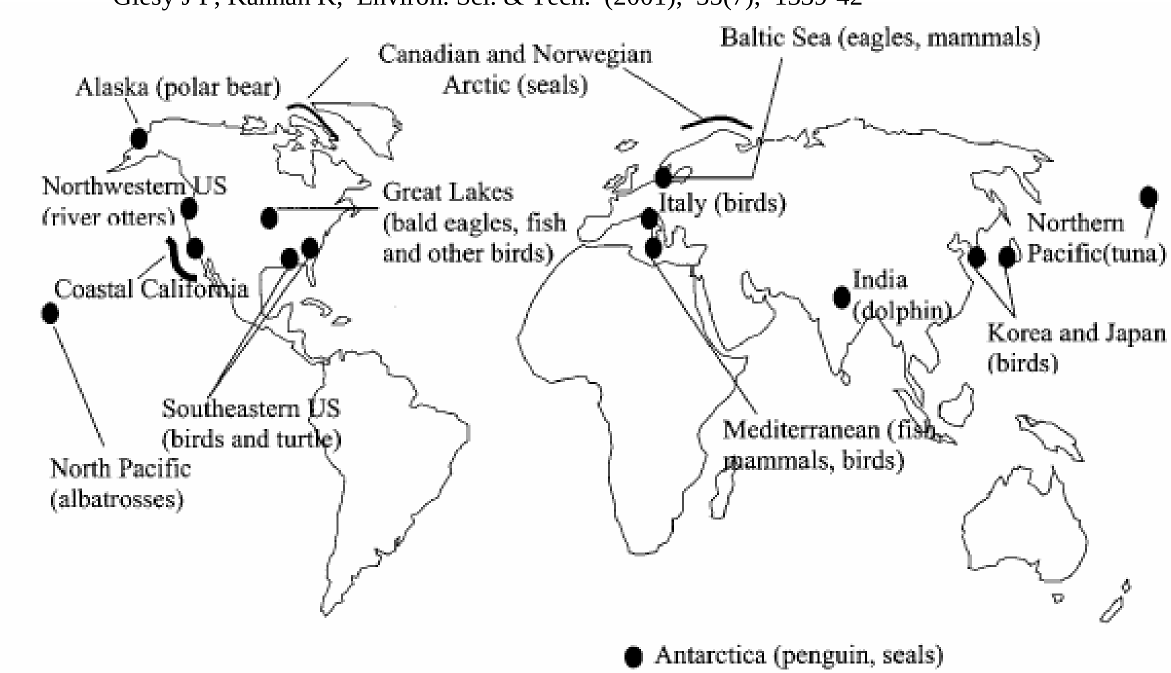
- Disadvantages
  - Low plasma etch resistance of F-containing structures
  - Surface compatibility: low surface energy
  - Low glass transition temperatures (Tg)
    - Difficult to keep sharp pattern shape
    - Low contrast

Reduce Fluorination

Perfluorinated octyl compounds have been shown to bioaccumulate and disrupt cellular functions

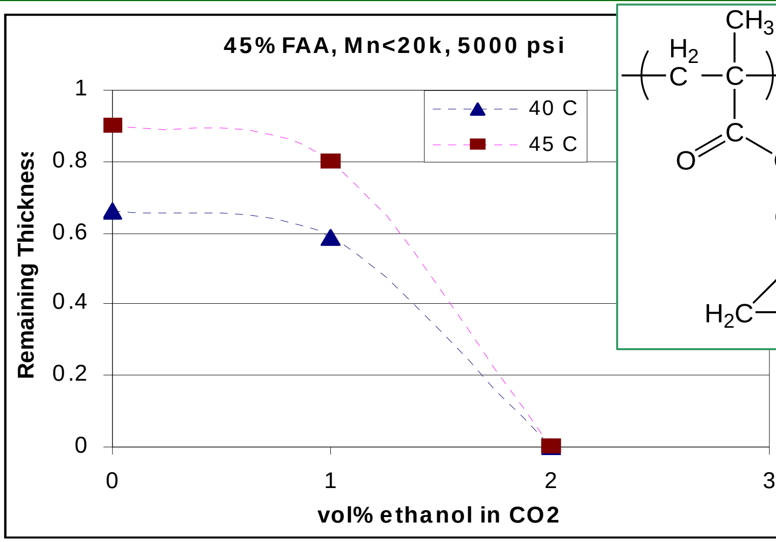
Environmentally friendly? → reduce need for fluorination

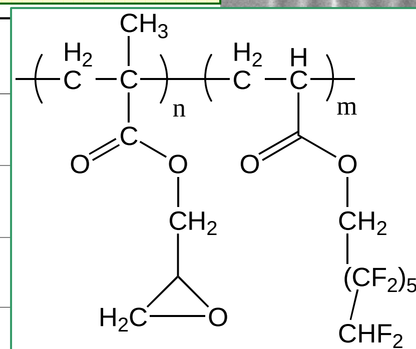
Giesy J P; Kannan K, Environ. Sci. & Tech. (2001), 35(7), 1339-42

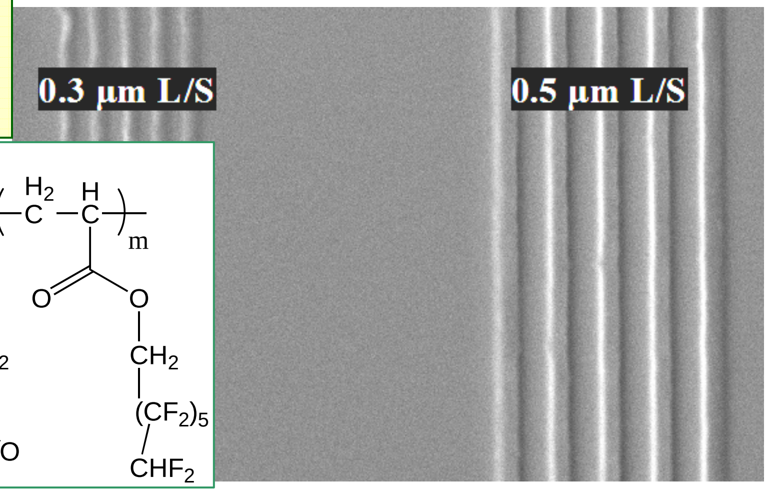


Reducing Fluorination: Using Cosolvents

- Increase solvent density
- Tune polarity of fluid
- Specific interaction with a comonomer





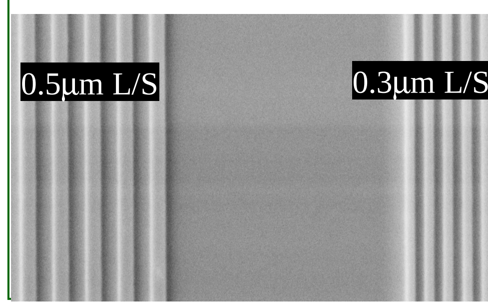


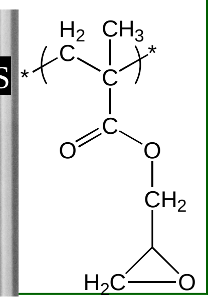
2 vol% ethanol (1.5mol%, 1.6wt%) in $scCO_2$

P = 5000 psi, T = 45ºC, t = 10 min

- 1vol% **ethanol**….very little effect
- 2vol% **ethanol**….100% removal

~2 vol% acetone





Mao, Yu; Felix, N. et al., *JVST B.*, **22**(5), 2004, 2473-8.

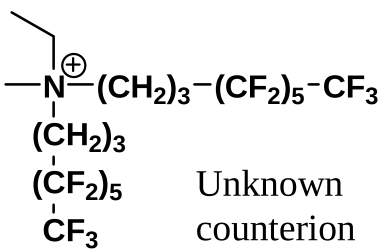
Additives for Processing Conventional Resists

- Patent literature full of examples of surfactant libraries used for $scCO_2$ dissolution of photoresists
  - Fluorinated or hydrocarbon tails
  - Polar or carboxylate heads
  - Mostly seen for pattern cleaning/drying

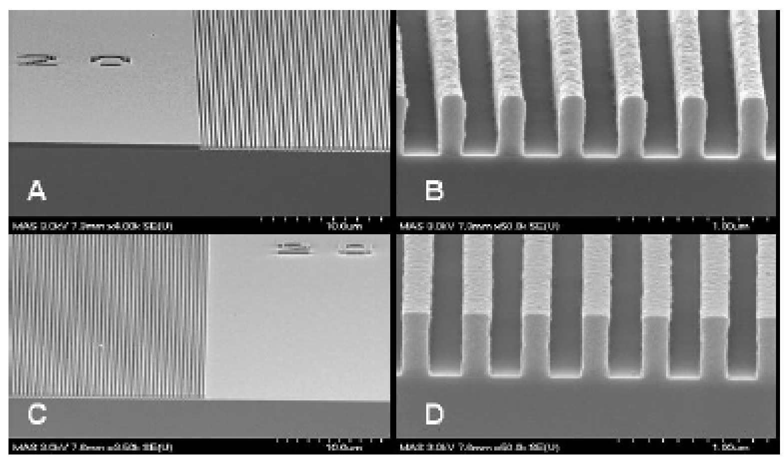
- Recent work by Micell Technologies on reactive ionic additives to impart $scCO_2$ solubility to conventional photoresists

‘CO_2 Compatible Salts’

- Rather than ionic surfactants, reactive fluorinated salts added to solution
  - Interact with weak acidic groups of photoresist to impart solubility
  - Due to lower amounts of acidic groups, unexposed regions gain sufficient solubility first
  - Presence of generated acid in exposed regions inhibits reaction with photoresist



Unknown counterion



Aqueous TMAH develop

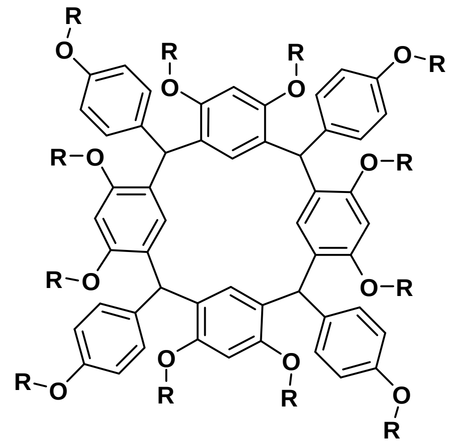
CO_2/CCS develop

Wagner, M., DeYoung, J., and C. Harbinson, SPIE v 6153 I 2006, p 61531.

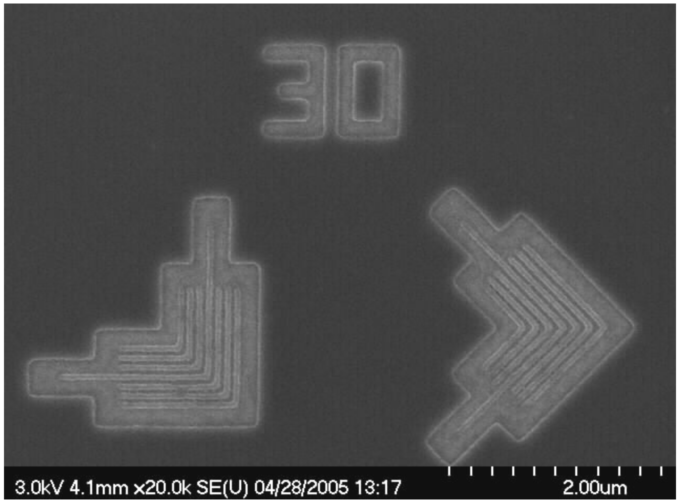
DeYoung, J., et al., SPIE v 6153 I 2006, p 615345.

Molecular Glass Photoresists

- Small molecule size ~1-2nm
- Well defined molecular structures
  - No distribution of mass
- Low tendency towards crystallization
  - bulky irregular shape or different conformation states
- Strong intermolecular attractive forces for high Tg
  - Specific interactions such as H-bonding



R = -H or -tBOC



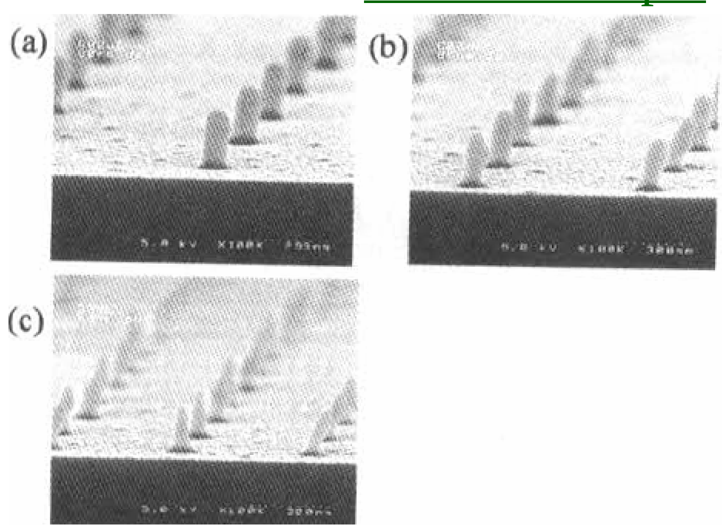
S. W. Chang, R. Ayothi, D. Bratton, D. Yang, N. Felix, H. B. Cao, H. Deng and C. K. Ober, *J. Mater. Chem.*, **16** (2006), 1470-74.

Images obtained at Lawrence Berkeley National Laboratories by EUV microexposure tool

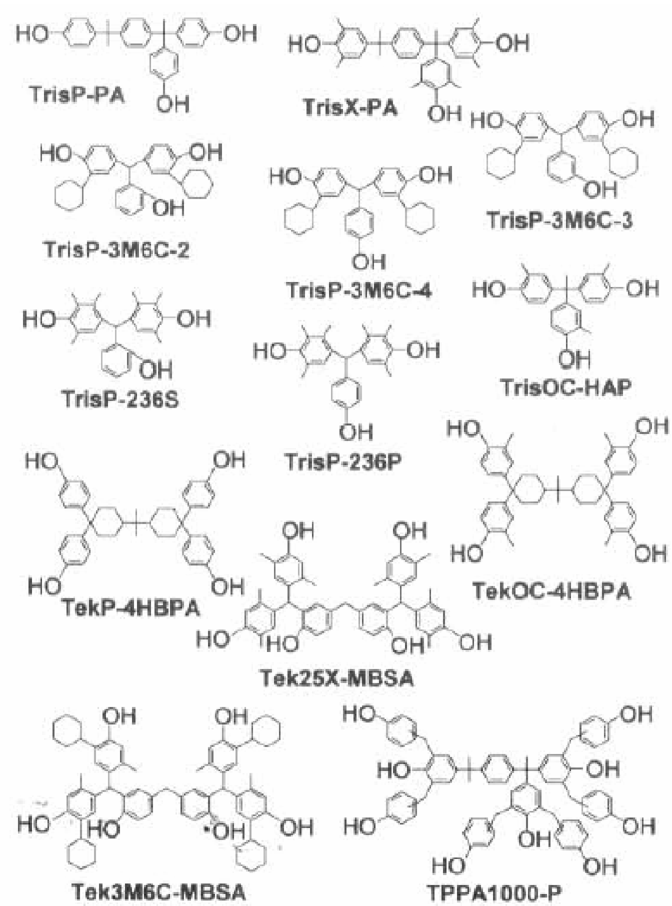
Molecular Glass Resist Solubility in scCO2

- Due to their small size, these resist materials have the potential for scCO2 solubility w/o fluorine
- Balance between size and polar functionality

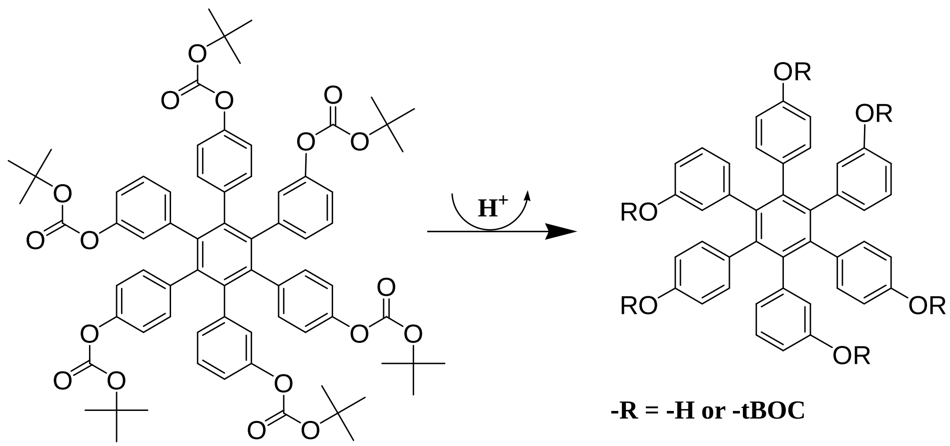
Recent example

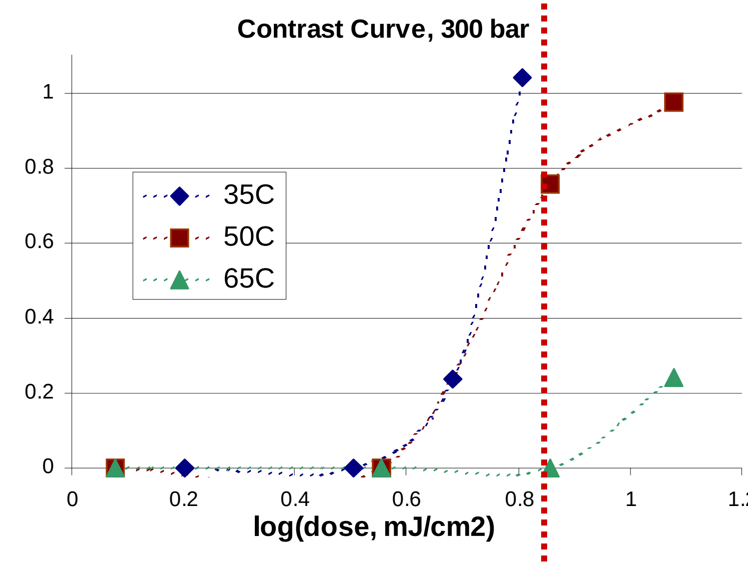


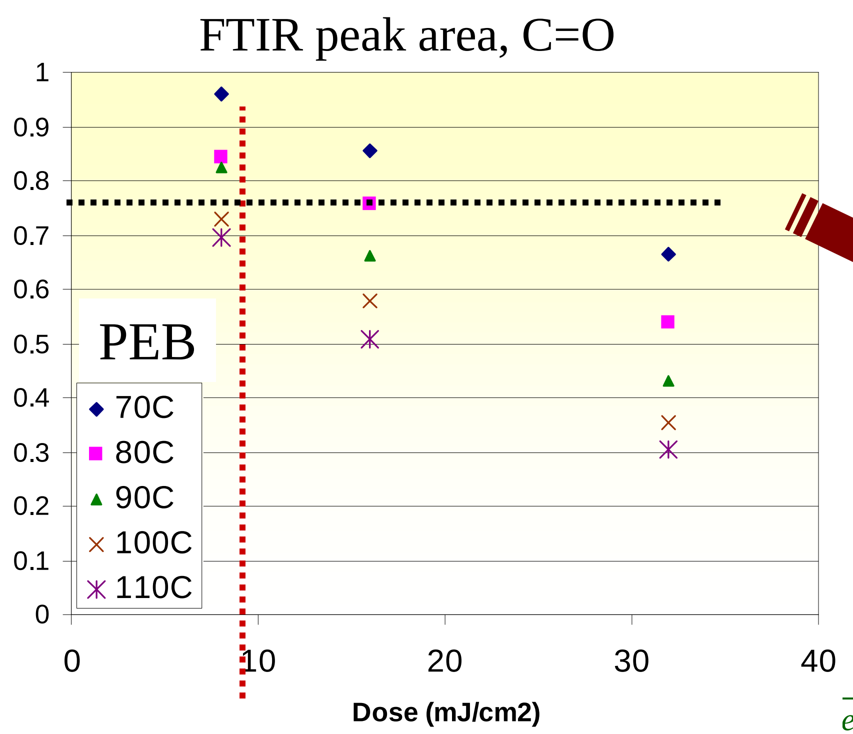
H. Shiraishi, J. Yamamoto, T. Sakamizu, *J. Photopolym. Sci. Technol.* **19**(3) (2006), 367-372.



Solubility Switching

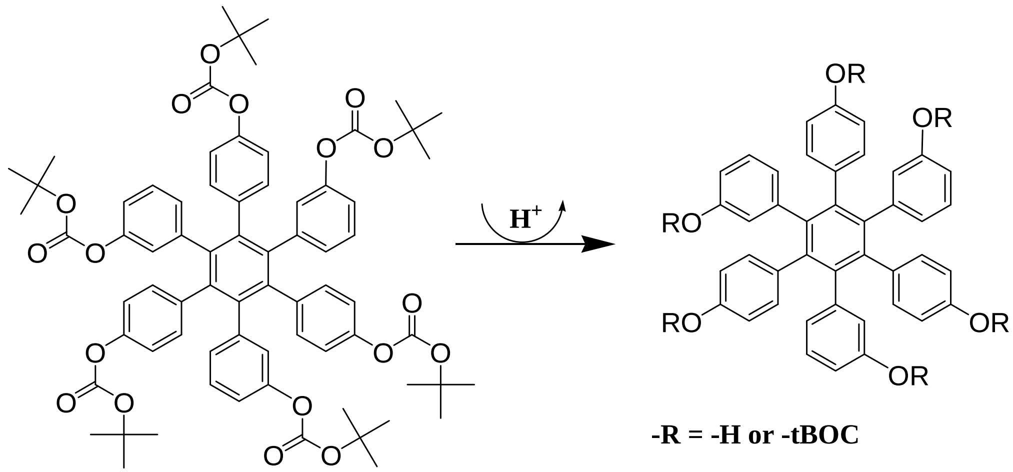


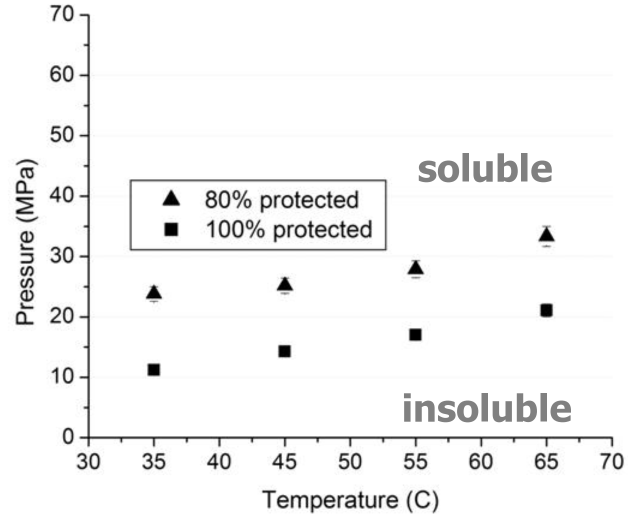


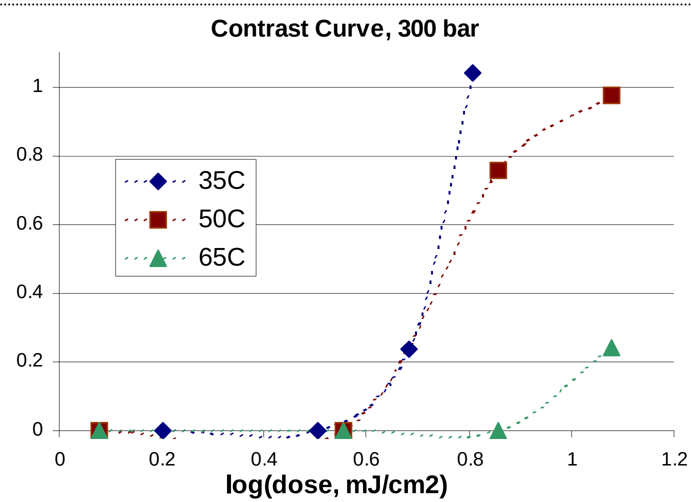


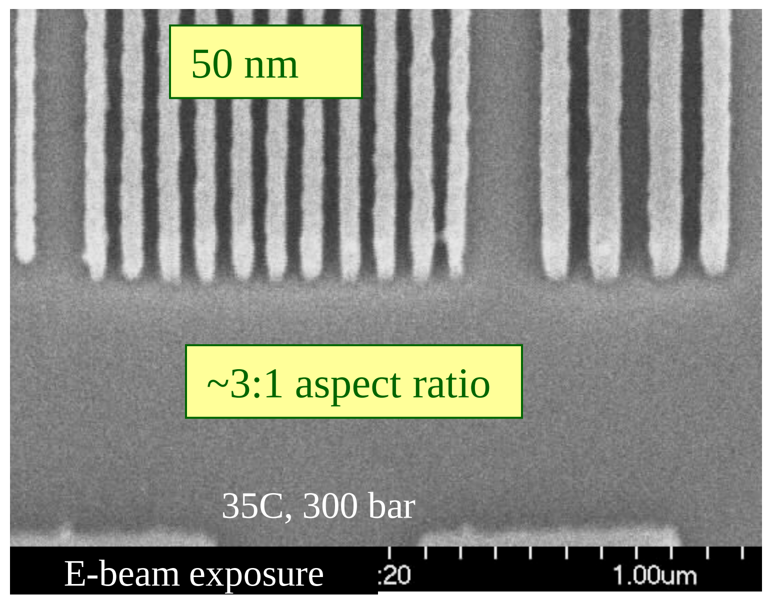
From FTIR data, solubility switch happens below <80% tBOC protection

High Resolution MG Resist for Supercritical CO_2



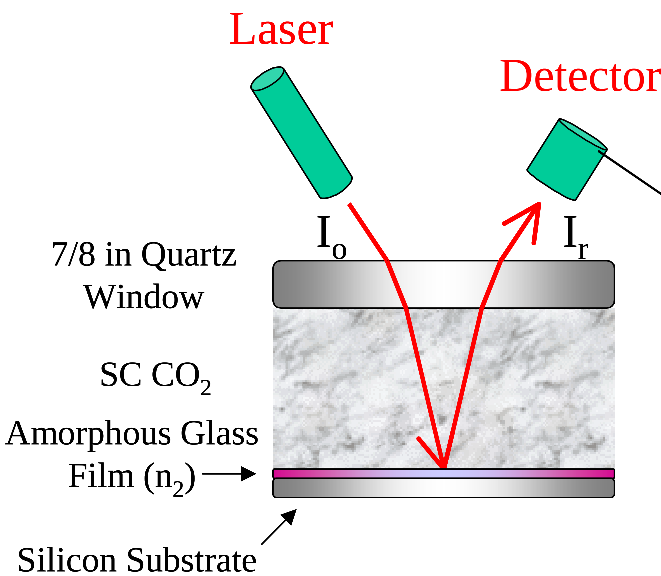


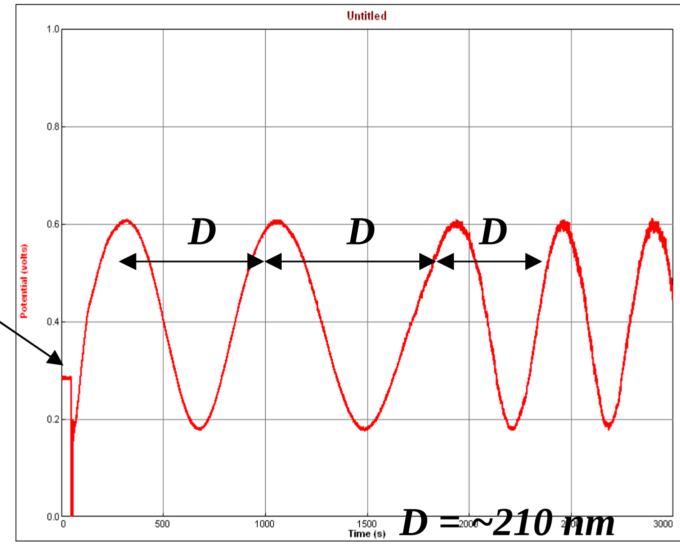


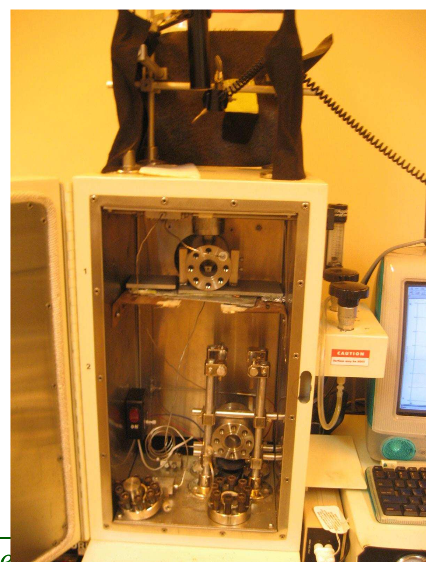


Felix, N. M, Tsuchiya, K., and C. K. Ober, *Adv. Mater.*, 18(4), 2006, p 442-446.

Dissolution Rate Measurments







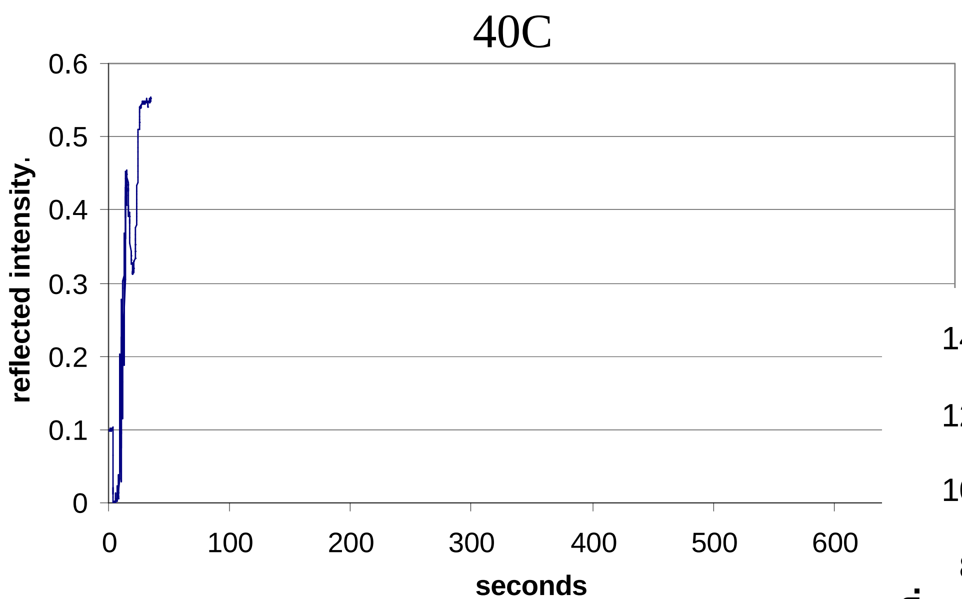
$$D = \frac{\lambda}{2\sqrt{n_2^2 - n_1^2 \sin^2(\theta)}}$$

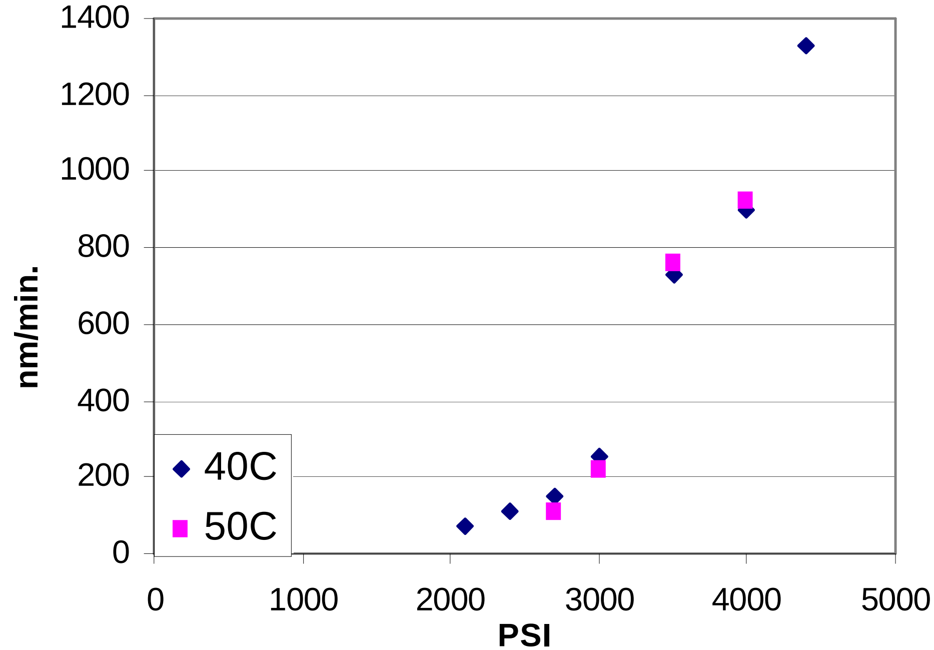
λ = 632.8 nm

n_1 = solvent refractive index

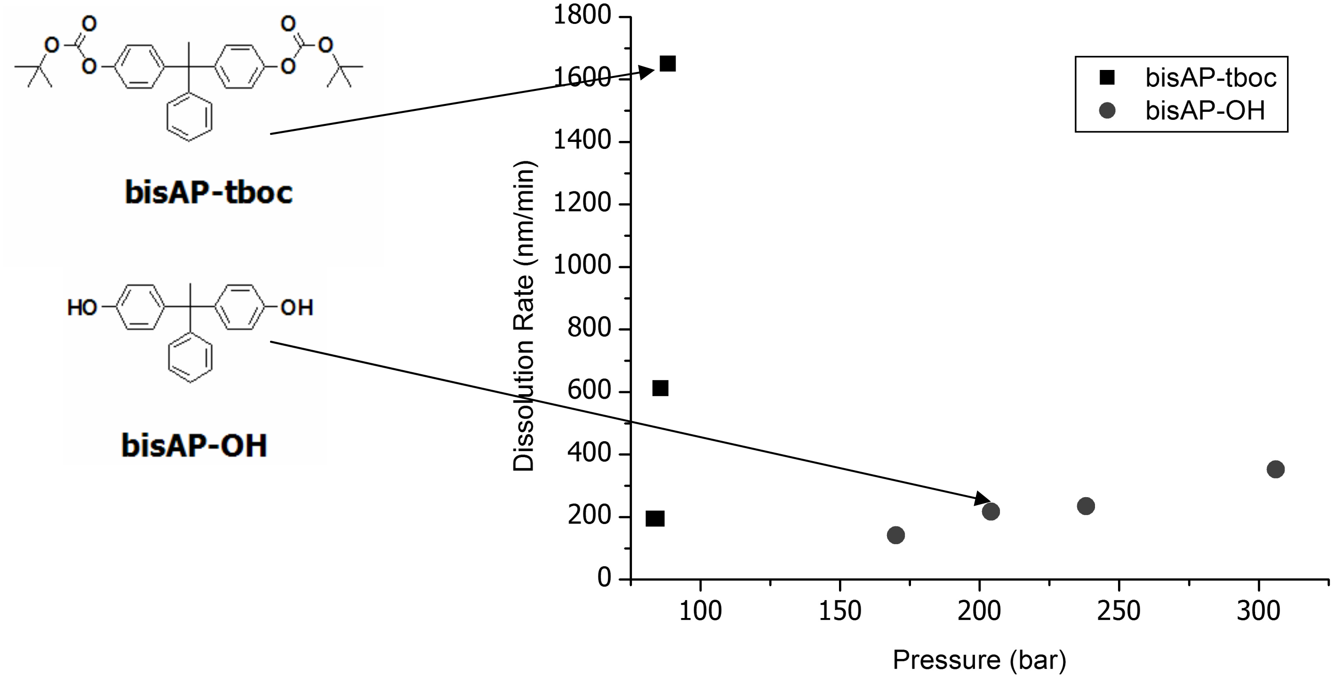
n_2 = film refractive index (~1.55)

Increasing pressure





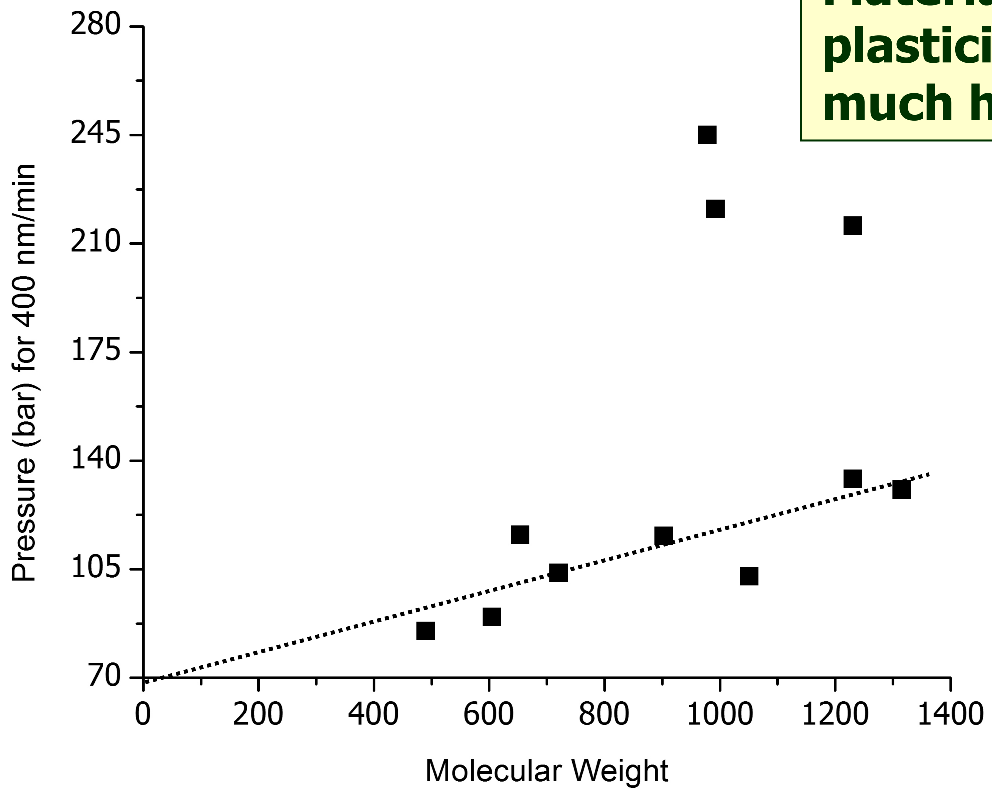
Effects of polarity



- **Molecules with less than 3 –OH groups still significantly soluble.**
- **Effect more pronounced at lower temperatures.**
- **Indicative of contrast between exposed and unexposed regions.**

Effect of molecular weight, Tg

Materials that resist plasticization require much higher pressures.



Necessary pressure to achieve dissolution rate increases predictably with larger MW.

However, photoresists approaching 2000 g/mol still soluble in $scCO_2$!

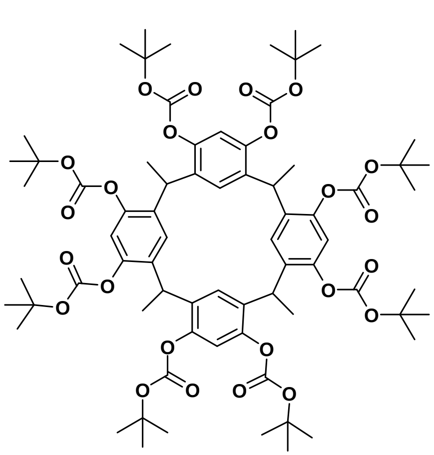
Felix, N. M, et al., *J. Mat. Chem.*, in press.

Going forward

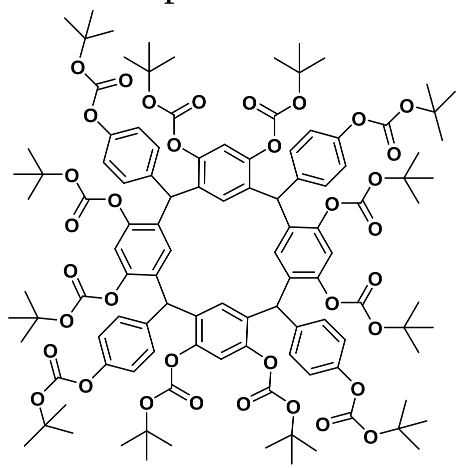
- Methodology in place for predicting, measuring $scCO_2$ solubility, especially with small molecules
  - Patterning possible with high Tg materials
- Can be expanded to positive-tone materials
  - Need chain-scission type resist materials

Calix[4]resorcinarenes

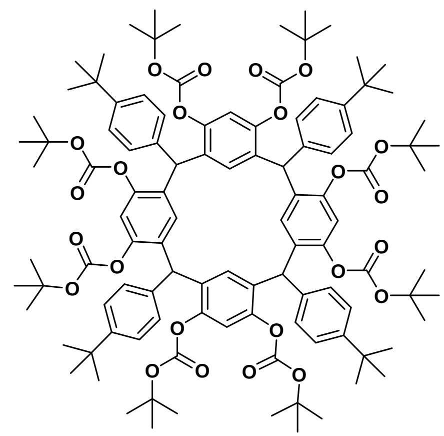
calix-tboc



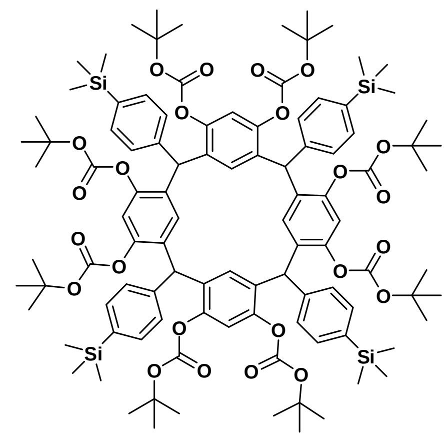
4hp-calix-tboc



4tb-calix-tboc

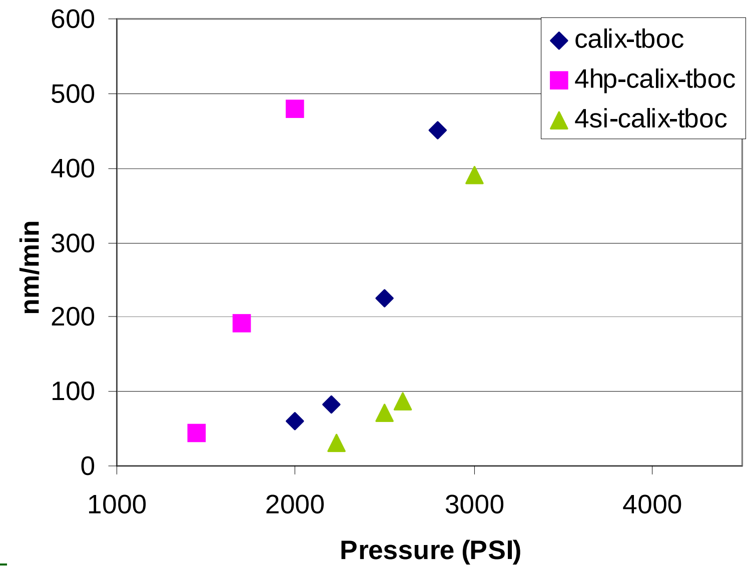


si-calix-tboc



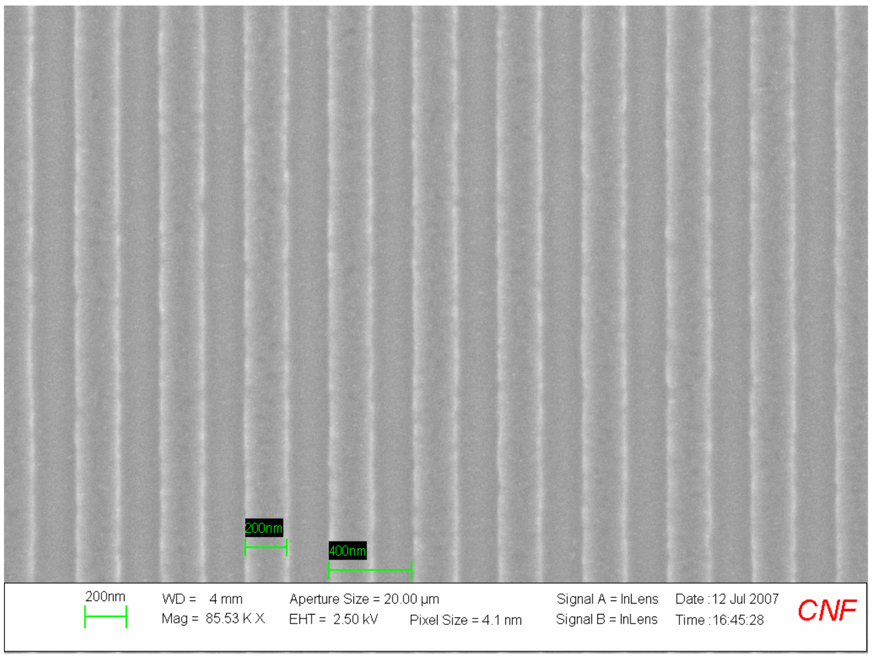
Felix, N. M, et al., *manuscript in preparation.*

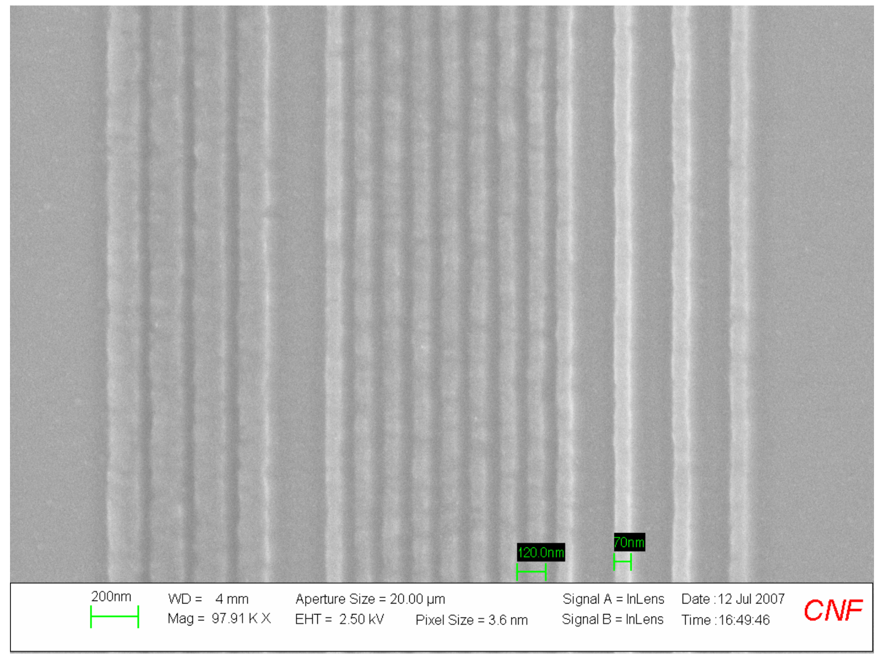
	Tg (C)
calix-tboc	**107**
4hp-calix-tboc	**84**
4tb-calix-tboc	**110**
4si-calix-tboc	**140**



Patterning

Developed 37C, 2500psi (e-beam)



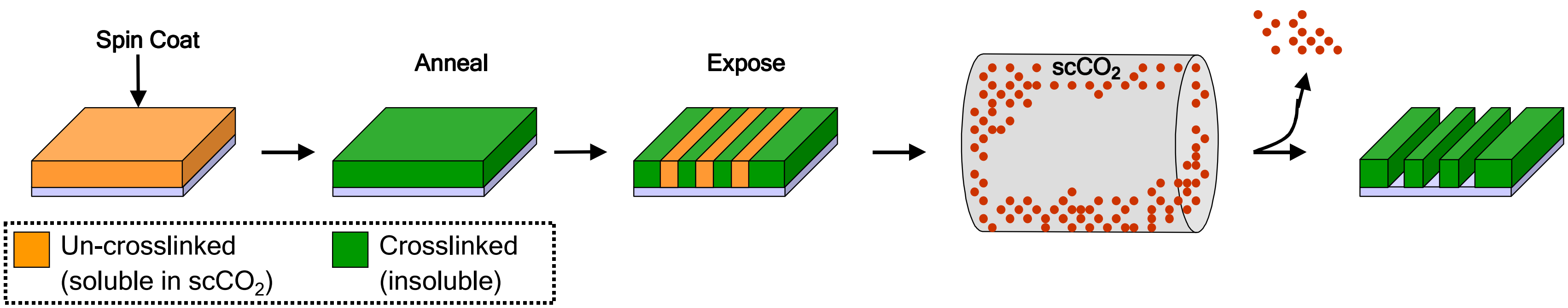


- As expected, sub-100nm performance shown with calix[4]resorcinarenes developed in scCO2

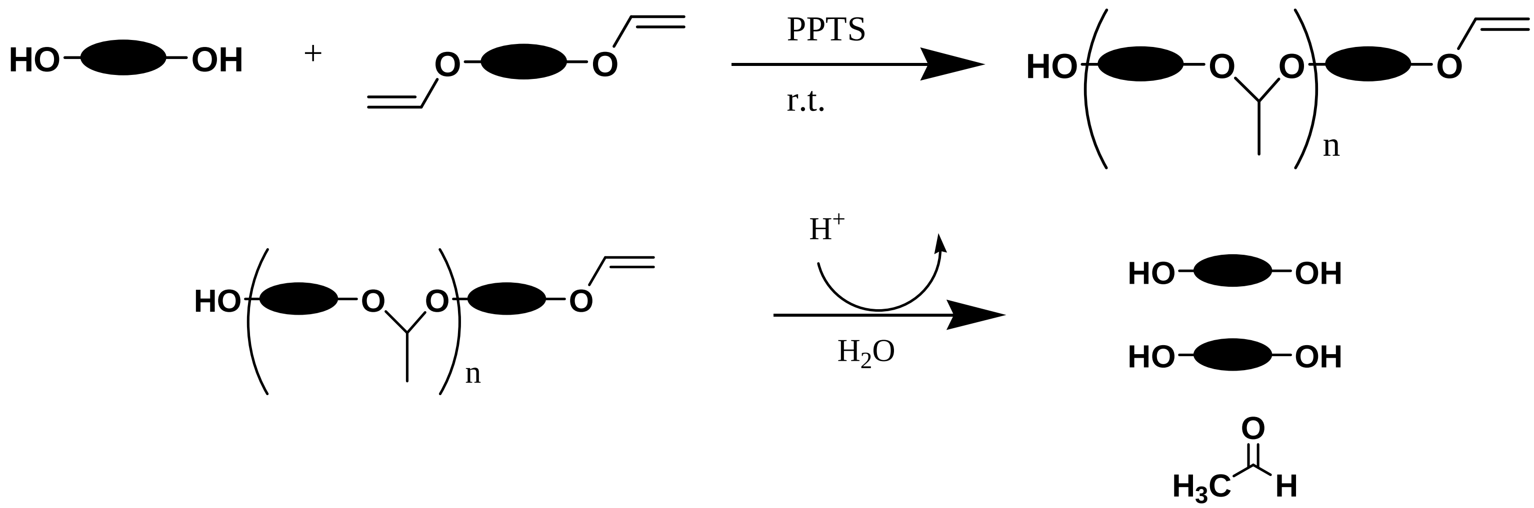
De-crosslinking Resists for Positive Tone

- PMMA is classic example
  - High resolution e-beam, EUV resist with low LER
  - Problem: low sensitivity

- Acid catalyzed de-crosslinking
  - Improved sensitivity
  - Use acetal bonds to crosslink otherwise $scCO_2$ soluble species

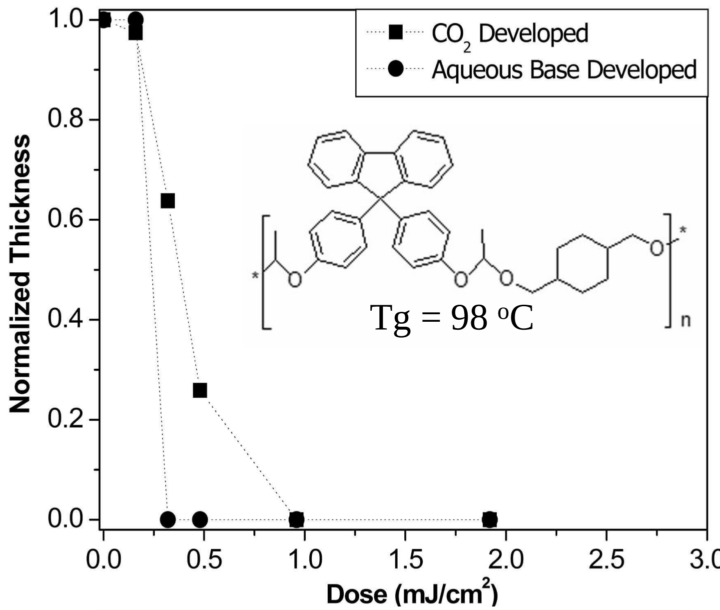


Acetal-backbone polymers

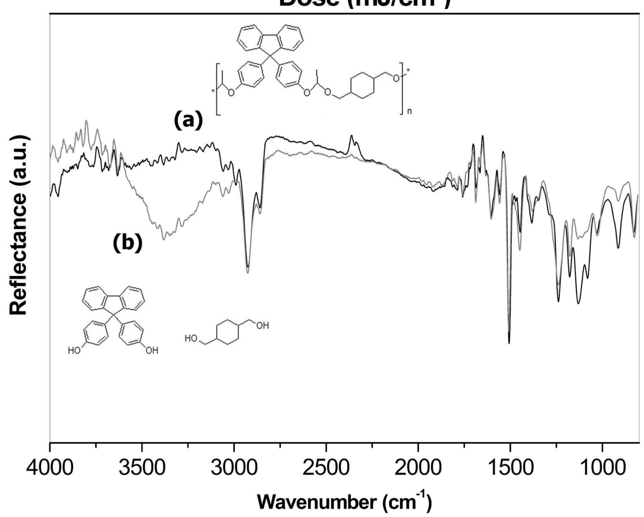


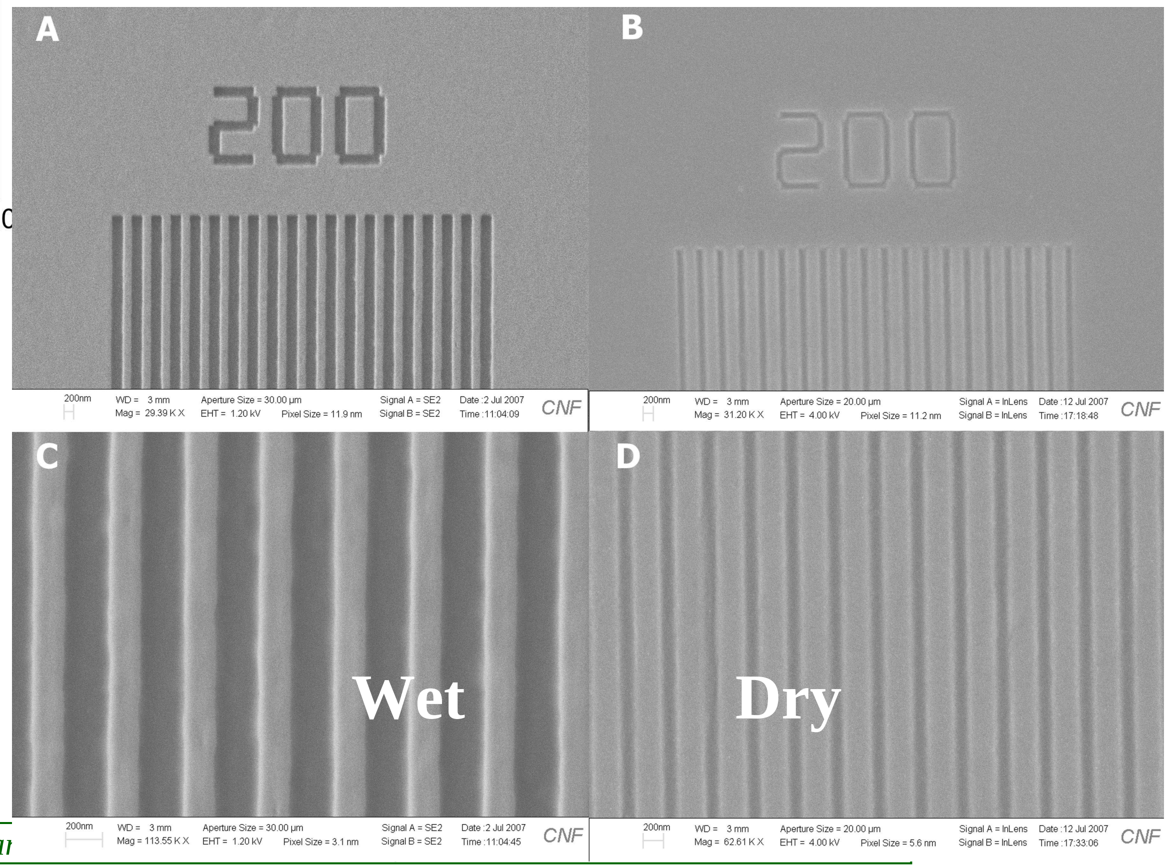
- Optimal system for scCO2 development
  - Bisphenol-type compounds shown to be scCO2-soluble
  - Large changes in molecular weight lead to solubility contrast

Patterning



- Electron-beam patterning, 100kV, Cornell
- Develop in scCO2: 40C, 2000 psi (140 bar)
- First intrinsic positive-tone system for scCO2 development!





Summary

- Along with being environmentally friendly, supercritical CO_2 shows performance advantages.
- Molecular glass photoresists have shown good performance, low LER under EUV patterning.
- Any given molecular glass platform has the potential for both base development and $scCO_2$ development.
  - Molecules approaching 2000 g/mol significantly soluble
  - < 65nm features shown with select systems
- First report of intrinsic positive-tone system for $scCO_2$ development.

Acknowledgements

- Funding
  - SRC/Sematech ERC for Environmentally Benign Semiconductor Manufaturing
- Facilities
  - Cornell Nanoscale Facility (CNF)
  - Cornell Cneter for Materials Research (CCMR)
- Folks
  - Prof. Chris Ober and entire Ober Group
    - Dr. Rama Ayothi
    - Kosuke Tsuchiya
    - Anuja De Silva
    - Camille Luk